SCIENCE FOR CERAMIC PRODUCTION

COMPOSITION AND AGGREGATIVE STATE OF PRODUCTS OF TITANIUM DIOXIDE HEATED IN AN ARGON MEDIUM

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The thermodynamic modeling methods are used to calculate the compositions of a condensed medium taking into account the existence of solid and liquid solutions of TiO_2, TiO, Ti_2O_3, Ti_3O_5, and Ti_4O_7, as well as partial pressures of $\{TiO_2\}$, $\{TiO\}$, $\{Ti\}$, $\{O_2\}$, and $\{O\}$ formed in heating initial titanium dioxide in an argon medium under a pressure of 9.8066×10^{-2} MPa in the temperature interval of $300 – 2485$ K. The obtained results can be useful for the high-temperature synthesis of complex ceramics with the participation of titanium dioxide and for analysis of the composition of ceramics.

Titanium dioxide is widely used as an initial component in the production of diverse types of ceramics that are promising materials for contemporary technologies. Such materials include complex oxide ceramics, glass ceramics, various ceramic composites, nanoceramics, etc. [1 – 3].

One of the main techniques in the synthesis of complex types of ceramics is the sintering of oxide mixtures. This process, as a rule, is implemented in nonequilibrium conditions, either in air, or in an atmosphere containing oxygen. Detailed studies of the compositions of such materials produced at different temperatures are often missing. In particular, it is believed [4] that TiO_2 retains a constant composition until its transition to a liquid state.

However, it cannot be excluded that chemical transformations occurring in heat treatment of mixtures containing TiO_2 may produce other types of titanium oxides which, in turn, are capable of participating in the formation of the composition and functional properties of target products.

The purpose of the present study is the thermodynamic analysis of products formed in heating TiO_2 in a wide temperature range: $\Delta T = 300 – 2485$ K.

In modeling products of TiO_2 thermal treatment we proceeded from the following assumptions.

It is known that the main condensed phases in the Ti – O system are five oxides, of which the most high-melting is TiO_2 with a melting point of 2185 K. The melting point of the other oxides are (K): 2110 for Ti_2O_3, 2050 for Ti_3O_5, 2030 for TiO, and 1960 for Ti_4O_7 [5].

The initial condensed medium was TiO_2; to prevent the effect of the gaseous phase, the computer experiment was performed in an argon medium under isobaric conditions: pressure 9.8066×10^{-2} MPa.

In heat-treating titanium dioxide we expected the possibility of formation of solid and liquid solutions of the initial TiO_2 and other titanium oxides: TiO, Ti_2O_3, Ti_3O_5, and Ti_4O_7.

Taking into account the melting temperatures of titanium oxides, we considered six systems for which the following condensed media were specified:

system I, $\Delta T = 300 – 1960$ K – solid solution of five titanium oxides;

system II, $\Delta T = 1960 – 2030$ K – solid solution ($TiO_2 + TiO + Ti_3O_5 + Ti_2O_3$) and liquid Ti_4O_7 phase;

system III, $\Delta T = 2030 – 2050$ K – solid solution ($TiO_2 + Ti_3O_5 + Ti_2O_3$) and liquid solution ($Ti_4O_7 + TiO$);

system IV, $\Delta T = 2050 – 2110$ K – solid solution ($TiO_2 + Ti_2O_3$) and liquid solution ($Ti_4O_7 + TiO + Ti_3O_5$);

system V, $\Delta T = 2110 – 2185$ K – solid phase TiO_2 and liquid solution ($Ti_4O_7 + TiO + Ti_3O_5 + Ti_2O_3$);

system VI, $\Delta T = 2185 – 2485$ K – liquid solution (melt) of all titanium oxides.

The volatile components of the gaseous phase that were taken into account were TiO_2, TiO, Ti, O_2, and O [4, 6]. Their thermodynamic characteristics are specified in [7]. The calculation has been performed according to the method described in [7, 8]. The software used was the ASTRA-4 package with the ASTRA.BAS database [7].

Condensed medium. It was found that the weight part of the most thermally stable TiO_2 remains prevalent in the con-

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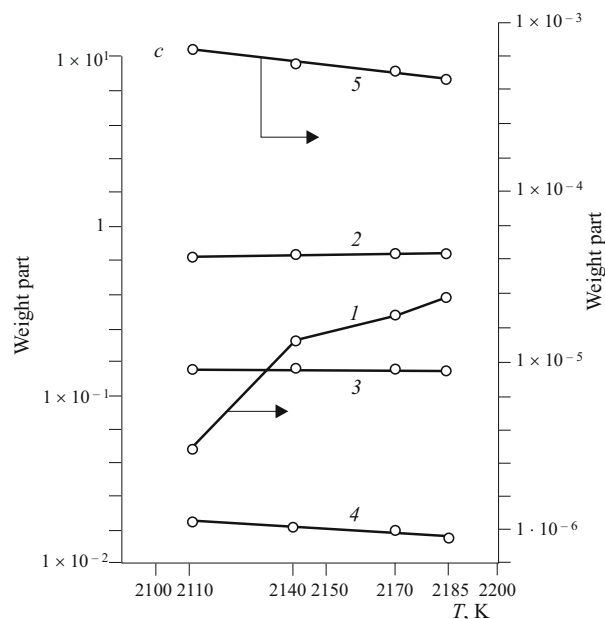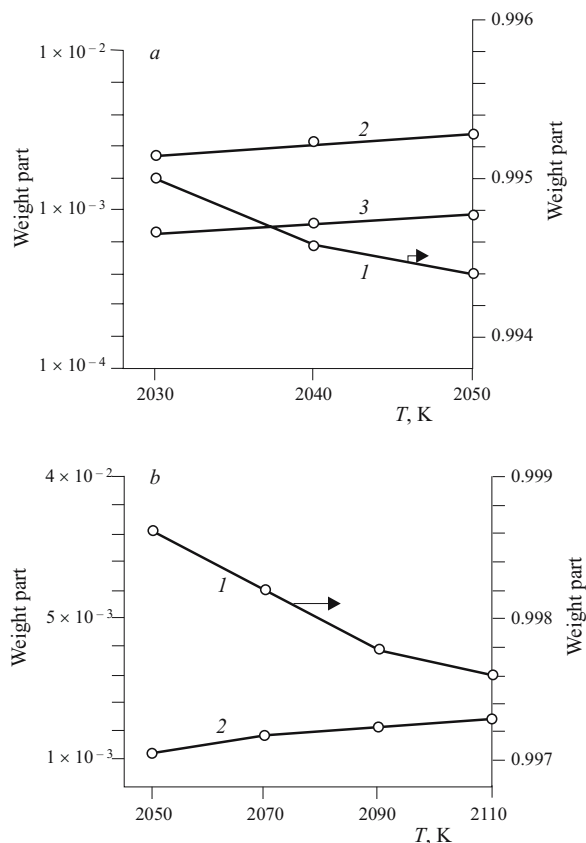[1] Institute of Metallurgy, Ekaterinburg, Russia; Institute of Chemistry of Solids, Ekaterinburg, Russia.

Fig. 1. Condense medium compositions: *a*) system III ($\Delta T = 2030 - 2050$ K), weight part TiO_2 (*1*), Ti_3O_5 (*2*), and Ti_2O_3 (*3*) in solid solution; *b*) system IV ($\Delta T = 2050 - 2110$ K), weight parts TiO (*1*) and Ti_2O_3 (*2*) in solid solution; *c*) system V ($\Delta T = 2110 - 2185$ K), weight part of liquid solution ($Ti_4O_7 + Ti_3O_5 + Ti_2O_3$) (*1*) in the condensed medium of solid TiO_2 + liquid solution, weight parts of Ti_4O_7 (*2*), Ti_3O_5 (*3*), Ti_2O_3 (*4*), and TiO (*5*) in the liquid solution.

densed medium in the whole temperature range. At $\Delta T = 1462 - 2485$ K it varies from 1 to approximately 0.986. At the same time, the analysis of particular systems has revealed several nonstandard peculiarities in the variations of the medium composition.

System I ($\Delta T = 300 - 1960$ K). Calculations have shown that at a temperature below 1462 K the total weight parts of the oxides (Ti_4O_7, Ti_3O_5, TiO, Ti_2O_3) constitute less that 10^{-4}; with temperature increasing in the interval of $1462 - 1960$ K they grow insignificantly but do not exceed 10^{-2}.

System II ($\Delta T = 1960 - 2030$ K). The liquid phase Ti_4O_7 is not formed. The weight parts of the oxides (Ti_3O_5, Ti_2O_3, TiO) in the solid solution increase with increasing temperature, but their total weight parts do not exceed 10^{-2} either.

System III ($\Delta T = 2030 - 2050$ K). The liquid solution (Ti_4O_7 + TiO) is not formed. A rise in temperature increases the weight parts of Ti_3O_5 and Ti_2O_3 in the solid solution, whereas the weight part of TiO_2 decreases (Fig. 1).

System IV ($\Delta T = 2050 - 2110$ K). The liquid solution (Ti_4O_7 + TiO + Ti_3O_5) is not formed. With increasing temperature the weight part of Ti_2O_3 in the solid solution grows and the weight part of TiO_2 decreases (Fig. 1).

System V ($\Delta T = 2110 - 2185$ K). The simultaneous presence of the solid phase TiO_2 and the liquid solution (Ti_4O_7 + TiO + Ti_3O_5 + Ti_2O_3) was identified. The weight part of the latter in the condensed medium at $2110 - 2185$ K grows from about 5×10^{-6} to about 5.4×10^{-5}. The weight parts of TiO and Ti_2O_3 in the solution decrease with increasing
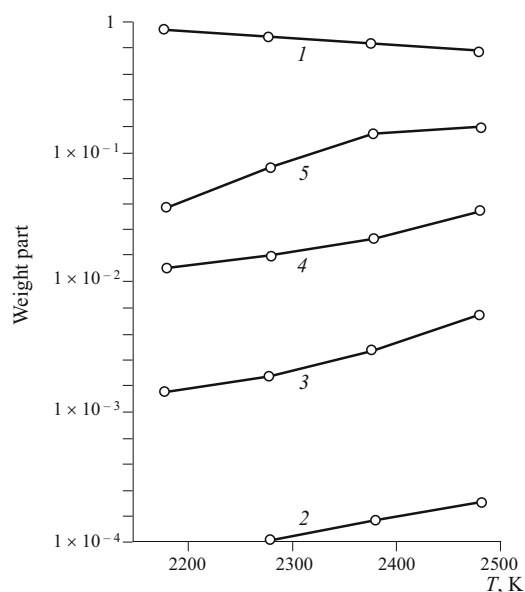
Fig. 2. Weight parts of TiO_2 (*1*), TiO (*2*), Ti_2O_3 (*3*), Ti_3O_5 (*4*), and Ti_4O_7 (*5*) in liquid solution in system VI ($\Delta T = 2185 - 2485$ K).

temperature, the weight part of Ti_4O_7 grows, and the weight part of Ti_3O_5 virtually does not change (Fig. 1).

System VI ($\Delta T = 2185 - 2485$ K). As the temperature increases, the weight part of TiO_2 in the liquid solution perceptibly decreases, whereas the weight parts of the other oxides

TABLE 1

ΔT, K	$\log p\,(\mathrm{O}) = A - B/T$		$\log p\,(\mathrm{O_2}) = A - B/T$		$\log p\,(\mathrm{Ti}) = A - B/T$		$\log p\,(\mathrm{TiO}) = A - B/T$		$\log p\,(\mathrm{TiO_2}) = A - B/T$	
	A	$-B$	A	$-B$	A	$-B$	A	$-B$	A	$-B$
1462 – 1960	4.775	20,098	3.510	13,596	–	–	9.993	43,711	8.096	31,038
1960 – 2030	4.696	20,227	3.404	13,778	10.570	58,636	9.555	43,352	7.914	30,682
2030 – 2050	4.715	20,270	3.385	13,750	10.591	58,666	9.761	42,958	7.844	30,541
2050 – 2110	4.479	20,195	2.969	13,713	10.975	58,637	10.030	43,100	7.805	30,461
2110 – 2185	13.724	42,978	21.453	59,266	– 7.543	13,010	0.746	20,235	7.767	30,380
2185 – 2485	3.810	17,722	1.599	8693	10.290	59,184	8.637	41,091	5.726	25,941

Note. The values of p_i in the computations are in MPa.
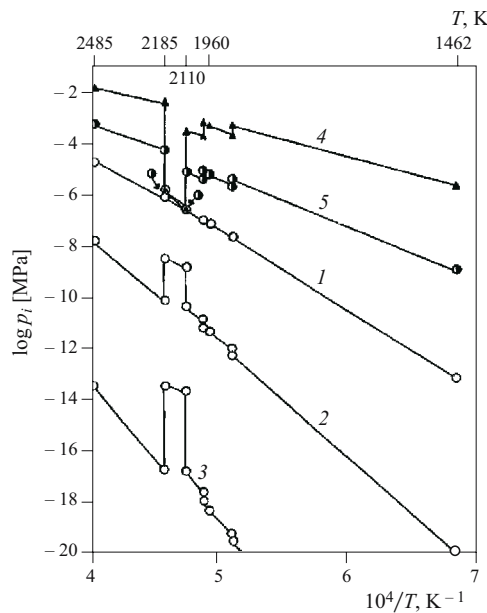
Fig. 3. Dependences of partial pressures of the gaseous phase components X [*1*) {TiO$_2$}, *2*) {TiO}, *3*) {Ti}, *4*) {O$_2$}, and *5*) {O}] formed under heating titanium dioxide in an argon medium in the temperature interval of 1462 – 2485 K.

(Ti$_4$O$_7$, Ti$_3$O$_5$, TiO, Ti$_2$O$_3$) as the solution components increase (Fig. 2).

Thus, the thermodynamic analysis indicates that the condensed medium formed in heating titanium dioxide in argon is not represented only by the initial oxide (TiO$_2$) in the solid or liquid state. For instance, at temperatures preceding the melting (system V) we have identified the range of coexistence of solid TiO$_2$ and the liquid solution consisting of different titanium oxides, which can be interpreted as an "extended" effect of titanium dioxide premelting.

The gaseous phase. The equations for estimating the partial pressures of the main components of the gaseous phase under heating initial titanium dioxide in an argon medium are given in Table 1. The temperature dependences of partial pressures p_i of the gaseous phase components {O$_2$}, {O}, {TiO}, {TiO$_2$}, and {Ti} (the computations are performed based on the equations given in Table 1) are presented in Fig. 3. It can be seen that with increasing temperature the values p_i actually grow monotonically. An exception is the

interval $\Delta T = 2030 – 2185$ K, where we observe a decrease in partial pressure of the gaseous phase components {O$_2$} and {O} and the growth in the p_i of the gaseous components TiO and Ti. This effect is the most perceptible in the range of premelting of solid TiO$_2$ ($\Delta T = 2110 – 2185$ K), i.e., under the temperatures of the coexistence of the solid phase TiO$_2$ and the liquid solution (Ti$_4$O$_7$ + Ti$_3$O$_5$ + Ti$_2$O$_3$ + TiO).

Thus, the method of thermodynamic modeling in a wide temperature interval (300 – 2485 K) was used to identify the compositions of the condensed medium and the gaseous phase under heating TiO$_2$ in an inert atmosphere taking into account the possibility of formation of solid and liquid solutions with the participation of other titanium oxides. The range of coexistence of the solid phase TiO$_2$ with the liquid solution (Ti$_4$O$_7$ + TiO + Ti$_3$O$_5$ + Ti$_2$O$_3$) was identified. The obtained results can be useful for describing chemical transformations in the high-temperature synthesis of complex ceramics with the participation of titanium dioxide and for analyzing the composition of these ceramics.

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